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Through-space interactions between face-to-face, center-to-edge oriented arenes: importance of polar–π effects

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Two series of conformationally restricted polycyclic compounds (**1**–**3** and **4**–**7**) have been synthesized as model systems for studying the through-space interactions between face-to-face, center-to-edge (parallel-offset) oriented arenes. These compounds feature different X substituents on one of the interacting rings. By monitoring the variation of the $\Delta G^{\neq}$ for the rotation around the aryl–aryl bond in **1**–**7** as a function of X by 2D [^{1}H,^{1}H] EXSY NMR spectroscopy, it was found that the barriers increase on passing from electron-donating to electron-withdrawing substituted derivatives. Quantum mechanical calculations [MP2/DVZ (2d,p)//B3LYP/DVZ(2d,p)] gave barrier values and variations in agreement with the experimental data. The results are consistent with a repulsive arene–arene interaction dominated by electrostatic effects.

Introduction

Through-space interactions between π-systems[1] are important because they play a major role in controlling disparate chemical phenomena including molecular recognition,[2] stereoselectivity of organic reactions,[3] nucleic acid and protein macroscopic structures,[4] aggregation of extended π-systems,[5] and crystal packing.[6] Several theoretical studies have been aimed at elucidating the nature of the arene–arene interactions in the simple case of the benzene dimer (Fig. 1).[1,7] From these works emerged

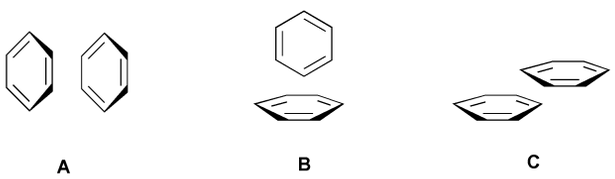


Fig. 1 Relative orientations of rings in the benzene dimer.

the idea that the parallel-stacked orientation **A** is unfavorable, the edge-to-face one **B** is favorable,[8] and the energy of the face-to-face, center-to-edge (parallel-offset) arrangement **C** depends on the contact surface area. A simple picture of the electronic distribution of benzene possessing a negatively charged core surrounded by a positively charged periphery,[7b,7i] rationalizes these results on an electrostatic basis.

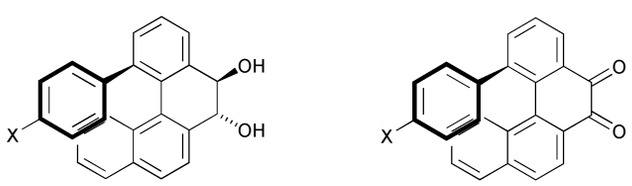
The electrostatic nature of the repulsive interaction in the parallel-stacked orientation **A** has experimentally been demonstrated by us by studying a number of variously substituted 1,8-diarylnaphthalenes,[9] and confirmed by work carried out on other systems.[10] These findings can be invoked to rationalize a variety of experimental results in different fields,[2–5] and nicely explain the tendency of the mixed arene–perfluoroarene systems to adopt the parallel-stacked orientation.[11]

Experimental work has also been devoted to elucidate the type **B** interaction between edge-to-face oriented arenes.[12,13] The results of a quantitative study led Hunter and coworkers to conclude that "the interactions between the CH groups of the edge ring and the π electron density of the face ring are sensitive to changes in the local charge distribution on the two rings".[12a,b] In contrast, Wilcox and coworkers[12c] designed a model system that was unresponsive to changes in arene substitution, a result that "casts substantial doubt on the importance of electrostatic interactions in edge-to-face binding events."[12c]

Face-to-face, center-to-edge interactions (type **C**), also called parallel-offset interactions, have received considerably less attention, despite the fact that this structural motif can be found in many structures.[14] Recently,[15,16] some conformationally flexible derivatives of *N*-benzyl-2-phenylpyridinium bromide adopting, among others, a parallel-offset conformation in water, have been reported. Herein, we investigate type **C** interactions in two conformationally restricted polycyclic systems.

Results and discussion

Synthesis. The model compounds **1**–**7** (Chart 1) were selected



1, X = OMe
2, X = H
3, X = NO_2

4, X = OMe
5, X = Me
6, X = H
7, X = F

Chart 1 Structures of compounds **1**–**7.**

to study type **C** interactions. These systems feature a reference ring with an electronic distribution that is constant across the series (*i.e.* the left-hand ring of the benzophenanthrene skeleton), and a rotating phenyl ring carrying electron-donating (ED) and electron-withdrawing (EW) substituents and partially overlapping the reference ring. The synthetic sequence for their preparation (Scheme 1) was planned so that **1**–**7** could be obtained from a common advanced intermediate.

Ullmann reaction between commercially available 2-bromo-3-nitrotoluene and 1-bromo-2-methylnaphthalene (3 mol equiv.)[17] gave the cross-coupling product **8** in 43% yield. Reduction of the nitro group (87% yield) followed by Sandmeyer

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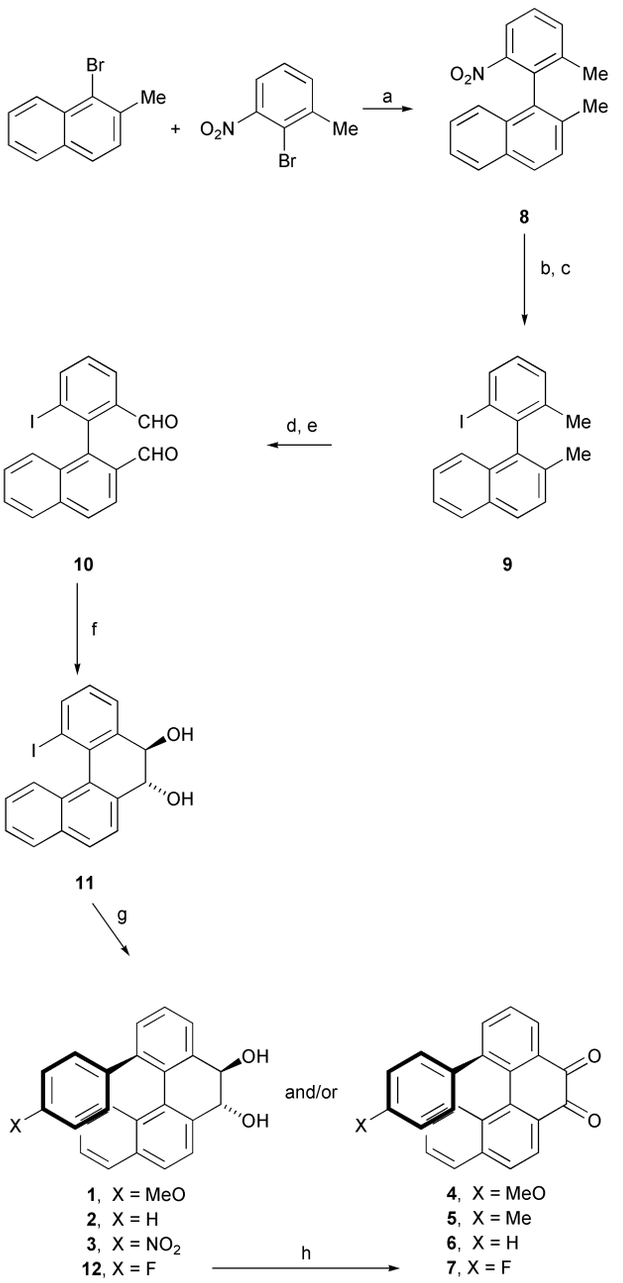

Scheme 1 Synthesis of compounds **1**–**7.** *Reagents and conditions*: a, Cu bronze, neat, 200 °C. b, $SnCl_2{\cdot}H_2O$, AcOEt, 80 °C, 15 h. c, H_2SO_4, $NaNO_2$, H_2O, 0–5 °C, 30 min; then KI 5 to 20 °C, 15 h. d, NBS cat. $PhCO_2O$, *hv*, CCl_4, 80 °C, 48 h. e, $AgNO_3$, dioxane, H_2O, 100 °C, 15 h. f, SmI_2, THF, −78 °C, 1 h. g, $Pd_2(dba)_3$, $AsPh_3$, DMF, 150 °C, 40 h. h, $PySO_3$, DMSO, RT, 2 h.

reaction of the resulting amine afforded the iodo compound **9** in 57% yield. Perbromination with excess NBS (5.5 mol equiv.) gave the bis(dibromomethyl) derivative (87% yield) that was then hydrolyzed to the corresponding bis(aldehyde) **10** by silver nitrate promoted reaction in dioxane–water (70% yield). Reductive intramolecular coupling carried out under McMurry conditions[18] to generate 1-iodobenzo[*c*]phenanthrene led to concomitant cleavage of the carbon–iodine bond. An attempt to prepare the same compound by reaction of **10** with hydrazine in acetic acid[19] failed, as did the synthesis of 1-iodo-5,6-epoxybenzo[*c*]phenanthrene by reaction of **10** with tris(dimethylaminophosphine) in toluene.[20] Ultimately, SmI_2[21] promoted pinacol reaction of **10** in THF at −78 °C gave the racemic diequatorial diol **11** (J = 10.5 Hz) in 75% yield.[22]

The reaction of **11** with 4X-substituted phenyl trimethylstannanes (4 mol equiv.)[23] in the presence of 0.2 mol equiv. of $Pd_2(dba)_3$ and 0.8 mol equiv. of $AsPh_3$[24] in degassed DMF

Table 1 $\Delta G^{\neq}$ for the rotation around the aryl–aryl bond in compounds **1**–**7** as determined by 2D EXSY ^{1}H NMR in THF-d_8 at the indicated temperature

Compound (type)	X substituent	$\Delta G^{\neq}$/kJ mol^{-1}	T/K
1 (diol)	MeO	47.9	195
2 (diol)	H	48.7	195
3 (diol)	NO_2	50.9	210
4 (dione)	MeO	51.0	210
5 (dione)	Me	51.7	210
6 (dione)	H	52.4	205
7 (dione)	F	53.1	210

(150 °C, 40 h) gave diols **1**–**3**, albeit in low yields (**1**, 29%; **2**, 12%; **3**, 11%). Surprisingly, **1** and **2** were accompanied by comparable amounts of the corresponding diketones **4** (24% yield) and **6** (11% yield). Starting from 4-methylphenyl trimethylstannane, diketone **5** was the only isolated product (15% yield). Finally, fluorodiketone **7** was obtained from the corresponding crude diol **12** (that could not be obtained in pure form) by $Py{\cdot}SO_3$ oxidation[25] in 12% overall yield from **11**.

Spectroscopy. The 300 MHz ^{1}H NMR spectra of **1**–**7** in THF-d_8 at RT revealed broad peaks for the protons of the 4X-substituted phenyl ring. Upon cooling the sample to about 200 K distinct resonances were observed with an average $\Delta\delta$ of 1.55 and 0.80 ppm for the *ortho* and *meta* protons, respectively. This result is consistent with rotation around the aryl–aryl bond in **1**–**7** occurring on an NMR timescale comparable to that of $\Delta\nu$ at RT but significantly more slowly at lower temperatures. The large $\Delta\delta$ seen for the *ortho* and *meta* protons suggests a preferred conformation where the 4X-substituted phenyl ring is frozen with one side of the ring above the shielding cone of the terminal ring of the benzophenanthrene system, *i.e.* a face-to-face center-to-edge conformation.[26]

The $\Delta G^{\neq}$ for the rotation around the aryl–aryl bond in the series of compounds **1**–**3** and **4**–**7** was determined by 2D [^{1}H,^{1}H] EXSY NMR experiments (Table 1).[27,28] The data for the diol and, independently, the diketone series show a trend for the barrier to rotation to increase from ED to EW X substituents on the phenyl ring. The plots of $\Delta G^{\neq}$ values *vs* the σ_{para} for **1**–**3** and **4**–**7** showed excellent linear relationship (Fig. 2).

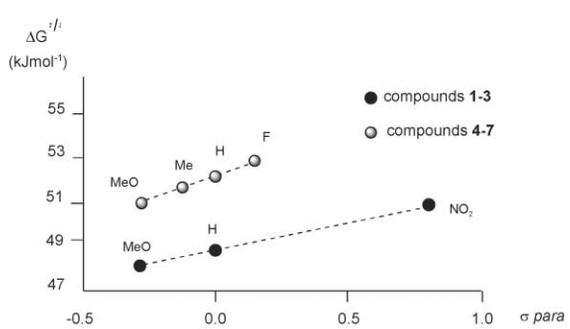

Fig. 2 Plots of $\Delta G^{\neq}$ (kJ mol^{-1}) *vs.* σ_{para} for compounds **1**–**3** (R = 0.9999) and **4**–**7** (R = 0.9998).

Also in type **A** interactions, the barrier to rotation around aryl–aryl bonds increased when the interacting rings were made less electron rich by the introduction of EW groups. This effect was apparently due to a decreased repulsion between the π electrons of the arenes at the ground state (GS) level.[9] In compounds **1**–**7**, the distance between the interacting rings is longer and the overlap between the π clouds is less extended than in the type **A** analogs previously studied.[9] Specifically, a typical angle between planes in **1**–**7** is *ca.* 55° with a center-to-center distance of 4.1 Å (closest contact 3.2 Å; furthest contact 5.2 Å). Thus, the repulsion between the π electrons is lower and the substituent effects should be less dramatic than previously seen. Indeed, the difference in the barriers between **1** and **3** is 3.0 kJ mol^{-1},

while in the 1,8-diarylnaphthalene case a similar change in substitution led to $\Delta\Delta G^{\neq}$ values of up to 14 kJ mol^{-1}.[9a] At the GS level compounds **1**–**7** should experience an attractive electrostatic interaction between the hydrogens of one ring and the π electrons of the other. However, the effect of different substituents on this interaction should be small,[12a] and the contribution of the CH–π factor to the overall interaction likely negligible.

Computation methods. Structural computations were performed with hybrid density functional methods (HDFT) using GAUSSIAN98.[29] The HDFT method employed Becke's 3 parameter functional[30] in combination with nonlocal correlation provided by the Lee–Yang–Parr expression[31] that contains both local and nonlocal terms, B3LYP. Dunning's DZV(2d,p)[32] double-ζ valence basis set was employed. These levels of theory have been previously shown to be reliable for structural determination in these types of compounds.[33] Single point energy computations were performed on optimized structures using MP2[34] dynamic correlation treatment giving superior energetic analysis.

Quantum mechanical calculations [MP2/DVZ (2d,p)// B3LYP/DVZ(2d,p)] on diketone **6** showed a centroid to centroid distance of 4.3 Å and a type **C** conformation between the reference and rotating rings in the GS. At the transition state (TS, 1 negative eigenvalue) calculations showed that one of the *ortho* hydrogens of the rotating ring points towards the carbon atom rim of the reference ring with a distance of *ca*. 2.2 Å; the same hydrogen is 2.8 Å from the center of the ring, significantly further than the rim-atom interaction. The computational barrier (TS–GS) is 48.2 kJ mol^{-1}, in reasonable agreement with experiment (52.4 kJ mol^{-1}). Thus the computation model supports the supposition that we are studying an interaction loosely analogous to type **C** in the series **1**–**7** and that this series behaves similarly to the type **A** analogs studied previously.[9]

Two additional derivatives of **6** were calculated: **6**-NH_2 and **6**-NO_2. They provide some perspective on the trends across a Hammett series. The predicted barriers to rotation for **6**-NH_2, **6**, and **6**–NO_2 are 47.5, 48.2, and 49.0 kJ mol^{-1}, respectively. Albeit a small effect, the barrier increases with decreasing donor character of the *para* substituent. This trend parallels the one experimentally observed for both the diketone and diol series, and the magnitude of the barriers is in accord with those measured by NMR, showing that the type **C** interactions can be modeled well by this level of theory.

Conclusions

In conclusion, both theory and experiments agree in indicating that aryl rotation is responsible for the spectral changes observed by the variable temperature NMR spectroscopy, and that the through-space (type **C**) interactions between parallel-offset oriented arenes is strongly influenced by electrostatic effects. Since these effects were also found to be important in the type **A** and type **B** interactions between parallel-stacked and center-to-edge oriented arenes, respectively, the results herein described lend additional support to the notion that polar–π interactions are decisive factors for understanding the arene–arene interactions.

Experimental

General. ^{1}H NMR spectra were recorded at 300 MHz in chloroform-*d* ($CDCl_3$) and were referenced to tetramethylsilane (TMS) at 0.00 ppm. ^{13}C NMR spectra were recorded at 75 MHz and were referenced to 77.0 ppm in $CDCl_3$. ^{19}F NMR spectra were recorded at 282 MHz in $CDCl_3$ and were referenced to hexafluorobenzene at 0.0 ppm. Variable temperature ^{1}H NMR spectra were recorded at 300 MHz in THF-d_8. IR spectra were recorded on thin films or as a solution in CH_2Cl_2. The 4-X-phenyl trimethylstannanes required for the synthesis of **1**–**7** were obtained from the corresponding 4-X substituted iodobenzenes following the reported procedure,[23] and were used as crude products.

2-Methyl-1-(2-methyl-6-nitrophenyl)naphthalene 8

To a stirred mixture of 1-bromo-2-methylnaphthalene (2.16 mL, 13.88 mmol) and copper bronze (2.93 g, 46.2 mmol) heated up to 200 °C, 2-bromo-3-nitrotoluene (1.0 g, 4.62 mmol) was added portionwise over a period of 6 h. After the end of the addition the mixture was stirred at 200 °C for 20 h, whereupon it was cooled to RT and acetone (20 mL) was added. The suspension was stirred for 1 h at RT and then filtered. The filtrate was concentrated under vacuum and the resulting crude product was purified by flash chromatography with a 95 : 5 hexanes : Et_2O mixture as eluant. The product, an orange thick oil, was isolated in 43% yield (0.556 g). IR (thin film): 3048, 2940, 1640, 1380, 1265 cm^{-1}. ^{1}H NMR: δ 7.87 (d, J = 7.9 Hz, 1H, hydrogen *ortho* to NO_2), 7.84 (dd, J = 8.9, 1.3 Hz, 1H, H–C5 of naphthalene), 7.81 (d, J = 8.9 Hz, 1H, H–C4 of naphthalene), 7.61 (d, J = 7.9 Hz, 1H, hydrogen *para* to NO_2), 7.50 (t, J = 7.9 Hz, 1H, hydrogen *meta* to NO_2), 7.47 (d, J = 8.9 Hz, 1H, H–C3 of naphthalene), 7.40 (dt, J = 8.9, 1.3 Hz, 1H, H–C6 of naphthalene), 7.31 (dt, 8.9, 1.3 Hz, 1H, H–C7 of naphthalene), 7.09 (dd, J = 8.9, 1.3 Hz, 1H, H–C8 of naphthalene), 2.15 (s, 3H, Me of naphthalene), 1.90 (s, 3H, Me of phenyl group); ^{13}C NMR: δ 148.0, 140.1, 134.3, 133.5, 133.2, 132.0, 131.9, 131.7, 128.5, 128.3, 128.25, 128.2, 126.5, 125.1, 124.3, 121.7, 20.1, 19.8. $C_{18}H_{15}NO_2$ requires: C, 77.96; H, 5.45; N, 5.05%; found: C, 77.77; H, 5.58; N, 4.97%.

3-Methyl-2-(2-methyl-1-naphthyl)aniline

A mixture of compound **8** (0.979 g, 3.53 mmol) and $SnCl_2$ dihydrate (4.0 g, 17.65 mmol) in refluxing ethyl acetate (50 mL) was stirred for *ca* 15 h. When TLC analysis showed the disappearance of the starting material, the mixture was cooled to RT and made slightly alkaline by the careful addition of a saturated aqueous solution of $NaHCO_3$. The mixture was then filtered on a Celite cake, the organic phase was separated, and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic phases were dried over $NaSO_4$, filtered and concentrated under vacuum. The crude product was purified by flash chromatography with a 80 : 20 hexanes : Et_2O mixture as eluant. The product, a yellow thick oil, was isolated in 87% yield (0.759 g). IR (thin film): 3469, 3388, 3053, 2950, 1612, 1265 cm^{-1}. ^{1}H NMR: δ 7.92 (d, J = 8.0 Hz, 1H, H–C5 of naphthalene), 7.87 (d, 8.4 Hz, 1H, H–C4 of naphthalene), 7.53 (d, J = 8.4 Hz, 1H, H–C3 of naphthalene), 7.50–7.40 (m, 3H, H–C6, H–C7 and H–C8 of naphthalene), 7.23 (t, J = 7.7 Hz, 1H, hydrogen *meta* to NH_2), 6.86 (d J = 7.7 Hz, 1H, hydrogen *para* to NH_2), 6.74 (d, J = 7.7 Hz, 1H, hydrogen *ortho* to NH_2), 2.29 (s, 3H, Me of naphthalene), 1.88 (s, 3H, Me of phenyl group); ^{13}C NMR: δ 144.2, 138.7, 134.8, 133.4, 132.6, 132.2, 129.0, 128.3, 128.1, 127.7, 126.4, 125.2, 125.0, 120.1, 112.8, 112.2, 24.0, 19.9. $C_{18}H_{17}N$ requires: C, 87.41; H, 6.93; N, 5.66%; found: C, 87.67; H, 7.11; N, 5.49%.

2-Methyl-1-(2-iodo-6-methylphenyl)naphthalene 9

To a stirred suspension of the above described amine (0.73 g, 2.95 mmol) in concentrated sulfuric acid (0.75 mL) and water (0.2 mL) cooled at −10 °C, a solution of sodium nitrite (0.305 g, 4.43 mmol) in water (0.2 mL) was added. After 15 min stirring at −10 °C, a solution of KI (1.45 g, 8.85 mmol) in water (0.6 mL) was slowly added. The deep red solution was stirred overnight while allowing the temperature to slowly rise to RT. The mixture was made neutral by the addition of a saturated aqueous solution of $NaHCO_3$, and was then washed with a saturated aqueous solution of Na_2SO_3 (10 mL). The resulting

mixture was extracted with Et_2O (2 × 20 mL) and CH_2Cl_2 (2 × 20 mL). The combined organic phases were dried over $NaSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography with hexanes as eluant. The product, a colorless oil, was obtained in 57% yield (0.602 g). IR (thin film): 3053, 2955, 1615, 1260 cm^{-1}. ^1H NMR: δ 7.91–7.86 (m, 2H, hydrogen *ortho* to I and H–C5 of naphthalene), 7.84 (d, J = 8.6, 1H, H–C4 of naphthalene), 7.44 (d, J = 8.6, 1H, H–C3 of naphthalene), 7.42 (dt, J = 8.0, 1.2 Hz, 1H, H–C6), 7.35 (dt, J = 8.0, 1.2 Hz, 1H, H–C7 of naphthalene), 7.33 (d, J = 8.0 Hz, 1H, hydrogen *para* to I), 7.15 (d, J = 8.0 Hz, 1H, H–C8 of naphthalene), 7.04 (t, J = 8.0 Hz, 1H, hydrogen *meta* to I), 2.13 (s, 3H, Me of naphthalene), 1.91 (s, 3H, Me of phenyl group); ^{13}C NMR: δ 144.2, 139.2, 138.7, 136.8, 132.9, 132.1, 131.3, 129.9, 129.1, 128.7, 128.0, 127.7, 126.3, 125.0, 124.6, 101.8, 20.3, 19.5. $C_{18}H_{15}I$ requires: C, 60.35; H, 4.22%; found: C, 60.58; H, 4.29%.

1-(2-Formyl-6-iodophenyl)-2-naphthaldehyde 10

This compound was prepared in two steps as follows. *First step*: A solution of compound **9** (0.147 g, 0.41 mmol), NBS (0.404 g, 2.25 mmol), and benzoylperoxide (0.003 g) in CCl_4 (4 mL) was refluxed overnight under a 150 W lamp. An additional portion of NBS (0.073 g, 0.41 mmol) was then added, and stirring was continued for 4 h. The suspension was filtered when still hot, and the filtrate was concentrated under vacuum. The residue was filtered through silica gel with a 80 : 20 hexanes : Et_2O mixture as eluant to give the product (0.245 g,) that was used without further purification in the following step. *Second step*: To a stirred, refluxing solution of the tetrabromide (0.387 g, 0.57 mmol) in dioxane (15 mL), a solution of silver nitrate (0.585 g, 3.44 mmol) in water (3.0 mL) was added dropwise. The resulting mixture was stirred at reflux overnight, and the precipitated silver bromide was then removed by filtration of the hot suspension. The filtrate was concentrated under vacuum, the residue was taken up into THF (7 mL), and a 10% aqueous solution of HCl (5 mL) was then added. The mixture was refluxed for 1 h, cooled down to RT, and extracted with Et_2O (3 × 20 mL). The combined organic phases were dried over $NaSO_4$, filtered, and concentrated under vacuum. The residue was dissolved in CH_2Cl_2 (20 mL) and anhydrous magnesium sulfate (1 g) was added. The suspension was then refluxed for 2 h under a Dean–Stark apparatus containing molecular sieves. The cooled solution was then concentrated under vacuum and the residue was purified by flash chromatography with a 70 : 30 hexanes : Et_2O mixture as eluant. The product, a pale yellow oil that becomes a waxeous solid when digested with pentane, was obtained in 70% yield (0.154 g). IR (thin film): 3050, 1692, 1620, cm^{-1}. ^1H NMR: δ 9.79 (s, 1H, CHO of phenyl group), 9.33 (s, 1H, CHO of naphthalene), 8.30 (dd, J = 8.0, 1.2 Hz, 1H, hydrogen *ortho* to I), 8.16 (dd, J = 8.0, 1.2 Hz, 1H, hydrogen *para* to I), 8.11 (AB system, J = 8.0 Hz, 2H, H–C3 and H–C4 of naphthalene), 8.00 (dd, J = 7.9, 1.2 Hz, 1H, H–C5), 7.67 (dt, J = 7.9, 1.2 Hz, 1H, H–C6 of naphthalene), 7.49 (dt, J = 7.9, 1.2 Hz, 1H, H–C7 of naphthalene), 7.45 (t, J = 8.0 Hz, 1H, hydrogen *meta* to I), 7.25 (dd, J = 7.9, 1.2 Hz, 1H, H–C8 of naphthalene); ^{13}C NMR: δ 190.7, 190.4, 144.5, 143.7, 143.4, 137.5, 136.0, 132.0, 131.8, 130.7, 130.0, 129.4, 128.7, 128.0, 127.9, 126.4, 122.8, 103.5. $C_{18}H_{11}I\ O_2$ requires: C, 55.98; H, 2.87%; found: C, 56.18; H, 2.78%.

***trans*-5-Iodo-9,10-dihydroxy-9,10-dihydrobenzo[*c*]phenanthrene 11**

To a solution of compound **10** (0.165 g, 0.43 mmol) in dry THF (7 mL) cooled at −78 °C and kept under a nitrogen atmosphere, a freshly opened 0.1 M solution of samarium diiodide in THF (9 mL) was added by syringe. After 30 min stirring at −78 °C, an additional 9 mL aliquot of samarium diiodide solution was added to the yellow solution, whereupon the color of the mixture became deep blue. Stirring was continued for 30 min at −78 °C and the reaction was quenched by the addition of a 10% aqueous solution of HCl (5 mL). After addition of Et_2O (20 mL) the organic phase was separated, washed with a saturated aqueous solution of Na_2SO_3 (10 mL), dried over $NaSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography first with 40 : 60 and then with 20 : 80 hexanes : Et_2O mixtures as eluants. The product, mp 155–157 °C, was obtained in 75% yield (0.125 g). IR (CH_2Cl_2): 3650, 3055, 2960, 1610, 1425, 1265 cm^{-1}. ^1H NMR: δ 7.84 (dd, J = 7.8, 1.2 Hz, 1H, H–C8 of naphthalene), 7.80 (d, J = 8.1 Hz, 1H, hydrogen *ortho* to I), 7.74 (br s, 2H, H–C4 and H–C3 of naphthalene), 7.71 (dd, J = 7.8, 1.2 Hz, 1H, H–C5 of naphthalene), 7.64 (d, J = 8.1 Hz, 1H, hydrogen *para* to I), 7.33–7.25 (m, 2H, H–C6 and H–C7 of naphthalene), 6.95 (t, J = 8.1 Hz, 1H, hydrogen *meta* to I), 4.44 (B part of AB system, J = 10.6 Hz, 1H, C*H*–OH bound to naphthalene), 4.23 (A part of AB system, J = 10.6 Hz, 1H, C*H*–OH bound to phenyl); ^{13}C NMR: δ 142.2, 139.9, 137.6, 136.3, 133.5, 130.2, 129.2, 129.2, 128.5, 128.4, 128.0, 125.5, 125.3, 124.3, 121.9, 96.8, 74.1, 74.0. $C_{18}H_{13}I\ O_2$ requires: C, 55.69; H, 3.37%; found: C, 55.78; H, 3.41%.

Synthesis of diols 1–3, 12 and diketones 4–6

General procedure. The synthesis of diol **1** and diketone **4** is illustrative of the procedure.

***trans*-5-(4-Methoxyphenyl)-9,10-dihydroxy-9,10-dihydrobenzo[*c*]phenanthrene 1 and 5-(4-methoxyphenyl)benzo[*c*]phenanthrene-9,10-dione 4**

To a solution of iodo compound **11** (0.065 g, 0.167 mmol) and 4-methoxyphenyltrimethylstannane (0.204 g, 0.713 mmol) in dry, degassed DMF (5 mL) kept under nitrogen, $Pd_2(dba)_3$ (0.0345 g, 0.0334 mmol) and $AsPh_3$ (0.041 g, 0.1336 mmol), both dissolved in degassed DMF (1 mL), were added in this order. The resulting mixture was stirred at reflux for 40 h. Most of the solvent was then evaporated under vacuum and the residue was dissolved in Et_2O (15 mL). The solution was washed with water (4 × 5 mL) to remove the remaining DMF, and the organic phase was dried over $NaSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography with pentane : Et_2O mixtures of increasing polarity as eluants (first eluant: 90 : 10; for diketone **4** isolation: 70 : 30; for diol **1** isolation: 30 : 70). Analytically pure samples were obtained by gravity chromatography of the diol and diketone compounds using flash chromatography silica gel as the stationary phase and the same eluants. Diol **1**, a white solid with mp 178–180 °C (decomp.) was obtained in 29% yield (0.0178 g). IR (CH_2Cl_2): 3650, 3054, 2987, 1422, 1264 cm^{-1}. ^1H NMR: δ 7.90–7.83 (m, 2H, H–C1 and H–C2), 7.73 (dd, J = 8.5, 1.3 Hz, 1H, H–C8), 7.64 (d, J = 8.4 Hz, 1H, H–C3′), 7.56–7.52 (m, 3H, H–C4′, H–C6, and H–C7), 7.16 (t, J = 8.4 Hz, 1H, H–C3″), 6.93 (dt, J = 8.4, 1.3 Hz, 1H, H–C4″), 6.91 (d, J = 8.9 Hz, 2H, hydrogen *meta* to methoxy in phenyl ring), 6.51 (d, J = 8.9 Hz, 2H, hydrogen *ortho* to methoxy in phenyl ring), 4.83 (B part of AB system, J = 10.5 Hz, 1H, H–C10), 4.58 (A part of AB system, J = 10.5 Hz, 1H, H–C9), 3.64 (s, 3H, *Me*O); ^{13}C NMR: δ 158.5, 140.5, 139.0, 135.7, 135.0, 133.2, 130.5, 130.0, 129.9, 128.7, 128.6, 128.5, 128.2, 127.3, 126.5, 124.9, 124.8, 121.9, 120.7, 113.5, 74.8, 74.6, 55.1. $C_{25}H_{20}O_3$ requires: C, 81.50; H, 5.47%; found: C, 81.37; H, 5.38%.

Diketone **4**, a red solid with mp 169–171 °C was obtained in 24% yield (0.0146 g). IR (CH_2Cl_2): 3040, 2964, 1682, 1514, 1252, 1031 cm^{-1}. ^1H NMR: δ 8.13 (dd, J = 8.5, 1.3 Hz, 1H, H–C8), 8.05 (B part of an AB system, J = 8.4 Hz, 1H, H–C1), 7.83 (dd, J = 8.5, 1.3 Hz, 1H, H–C6), 7.81 (B part of an AB system, J = 8.4 Hz, 1H, H–C2), 7.68 (dd, J = 8.4, 1.2 Hz, 1H, H–C4′), 7.62 (d, J = 8.4 Hz, 1H, H–C3′), 7.60 (t, J = 8.4 Hz, 1H, H–C7), 7.32 (dt, J = 8.4, 1.0 Hz, H–C3″), 7.00 (dt, J = 8.4, 1.0 Hz, H–C4″), 6.92 (broad multiplet, 2H, hydrogens *meta* to

MeO in phenyl ring), 6.55 (d, J = 8.9 Hz, 2H, hydrogens *ortho* to methoxy in phenyl ring), 3.66 (s, 3H, *Me*O); ^{13}C NMR: δ 184.0, 159.8, 142.7, 139.2, 138.2, 137.2, 135.0, 133.5, 131.9, 130.2, 130.0, 129.8, 129.4, 128.9, 128.8, 128.3, 127.7, 127.5, 126.1, 122.6, 113.2, 55.2. $C_{25}H_{16}O_3$ requires: C, 82.40; H, 4.43%; found: C, 82.37; H, 4.58%.

trans-5-Phenyl--9,10-dihydroxy-9,10-dihydrobenzo[*c*]phenanthrene 2

A white solid with mp 180–183 °C, was obtained in 12% yield. IR (CH_2Cl_2): 3655, 3055, 2986, 1422, 1264 cm^{-1}. ^{1}H NMR: δ 7.92–7.82 (m, 2H, H–C1 and H–C2), 7.77 (d, J = 8.5 Hz, 1H, H–C8), 7.66 (d, J = 8.4 Hz, 1H, H–C3′), 7.60–7.50 (m, 3H, H–C4″, H–C6 and H–C7), 7.15 (t, J = 8.4 Hz, 1H, H–C3″), 7.00–6.93 (broad multiplet, 5H of phenyl ring), 6.90 (t, J = 8.4 Hz, 1H, H–C4″), 4.87 (B part of AB system, J = 10.5 Hz, 1H, H–C10), 4.60 (A part of AB system, J = 10.5 Hz, 1H, H–C9); ^{13}C NMR: δ 142.5, 140.5, 139.2, 135.5, 133.0, 130.7, 130.0, 128.9, 128.8, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 126.3, 124.9, 124.8, 122.4, 120.8, 74.6, 74.5. $C_{24}H_{18}O_2$ requires: C, 85.18; H, 5.36%; found: C, 85.41; H, 5.29%.

5-Phenylbenzo[*c*]phenanthrene-9,10-dione 6

An orange solid with mp 138–140 °C (decomp.) was obtained in 11% yield. IR (CH_2Cl_2): 3050, 2960, 1682, 1510, 1250, 1025 cm^{-1}. ^{1}H NMR: δ 8.15 (dd, J = 8.0, 1.4 Hz, 1H, H–C8), 8.07 (B part of an AB system, J = 8.5 Hz, 1H, H–C1), 7.86 (dd, J = 8.0, 1.4 Hz, 1H, H–C6), 7.81 (A part of an AB system, J = 8.5 Hz, 1H, H–C2), 7.68 (dd, J = 8.4, 1.0 Hz, 1H, H–C4′), 7.63 (t, J = 8.0 Hz, 1H, H–C7), 7.62 (d, J = 8.0 Hz, 1H, H–C3′), 7.29 (dt, J = 8.0, 1.0 Hz, 1H, H–C3″), 7.07–7.00 (broad multiplet, 5H of phenyl ring), 6.97 (dt, J = 8.0, 1.0 Hz, 1H, H–C4″); ^{13}C NMR: δ 184.0, 143.5, 140.0, 139.2, 138.4, 137.5, 135.9, 132.5, 129.9, 129.8, 129.4, 129.1, 129.0, 128.9, 128.7, 128.4, 127.7, 127.4, 127.2, 126.2, 122.6. $C_{24}H_{14}O_2$ requires: C, 86.21; H, 4.22%; found: C, 85.99; H, 4.39%.

trans-5-(4-Nitrophenyl)--9,10-dihydroxy-9,10-dihydrobenzo[*c*]phenanthrene 3

A red solid with mp >200 °C was obtained in 11% yield. IR (CH_2Cl_2): 3650, 3053, 2986, 1423, 1266, 1045 cm^{-1}. ^{1}H NMR: δ 7.93–7.89 (m, 2H, H–C1 and H–C2), 7.88 (d, J = 8.5 Hz, H–C8), 7.83 (d, J = 8.8 Hz, 2H, hydrogens *ortho* to NO_2 in phenyl ring), 7.67 (d, J = 8.1 Hz, H–C3′), 7.60 (t, J = 8.5 Hz, 1H, H–C7), 7.53 (d, 8.5 Hz, 1H, H–C6), 7.45 (d, J = 8.1 Hz, 1H, H–C4′), 7.17–7.12 (m, 3H, H–C3″ and hydrogens *meta* to NO_2 in phenyl ring), 6.92 (t, J = 8.1 Hz, 1H, H–C4″), 4.86 (B part of AB system, J = 10.5 Hz, 1H, H–C10), 4.62 (A part of AB system, J = 10.5 Hz, 1H, H–C9); ^{13}C NMR: δ 149.5, 146.2, 140.5, 140.0, 136.2, 133.4, 130.5, 130.3, 129.5, 129.3, 128.5, 128.1, 128.0, 125.7, 125.3, 125.2, 124.2, 124.1, 123.2, 121.1, 74.6, 74.5. $C_{24}H_{17}NO_4$ requires: C, 75.20; H, 4.47; N, 3.65%; found: C, 75.49; H, 4.56; N, 3.59%.

5-(4-Methylphenyl)benzo[*c*]phenanthrene-9,10-dione 5

An orange solid with mp 115–117 °C was obtained in 15% yield. IR (CH_2Cl_2): 3055, 2988, 1684, 1488, 1266 cm^{-1}. ^{1}H NMR: δ 8.12 (dd, J = 8.5, 1.3 Hz, 1H, H–C8), 8.05 (B part of an AB system, J = 8.4 Hz, 1H, H–C1), 7.82 (dd, J = 8.5, 1.3 Hz, 1H, H–C6), 7.80 (A part of an AB system, J = 8.5 Hz, 1H, H–C2), 7.68 (d, J = 8.4 Hz, 1H, H–C4′), 7.63 (d, J = 8.4 Hz, 1H, H–C3′), 7.60 (t, J = 8.4 Hz, 1H, H–C7), 7.28 (dt, J = 8.4, 1.0 Hz, H–C3″), 6.97 (dt, J = 8.4, 1.0 Hz, H–C4″), 6.88 (broad multiplet, 2H, hydrogens *meta* to Me in phenyl ring), 6.80 (A part of an AB system, J = 8.8 Hz, 2H, hydrogens *ortho* to Me in phenyl ring), 2.13 (s, 3H, Me in phenyl ring); ^{13}C NMR: δ 184.0, 143.0, 139.2, 138.5, 138.3, 137.5, 137.1, 135.2, 131.9, 129.9, 129.8, 129.4, 129.1, 129.0, 128.9, 128.8, 128.5, 127.7, 127.5, 126.1, 122.6, 22.2. $C_{25}H_{16}O_2$ requires: C, 86.19; H, 4.63%; found: C, 86.28; H, 4.66%.

5-(4-Fluorophenyl)benzo[*c*]phenanthrene-9,10-dione 7

The inseparable mixture of crude diketone **7** and diol **12**, obtained as described above, was subjected to the following procedure: To a stirred mixture of **7** and **12** (0.016 g, approximately 0.045 mmol) in dry DMSO (0.5 mL) kept at RT under nitrogen, triethylamine (0.022 mL, 0.16 mmol) was added, followed by Py·SO_3 (0.0178 g, 0.112 mmol) in 0.5 mL of dry DMSO. After 5 h stirring at RT, the reaction was quenched by the addition of water (5 mL), and the solution was extracted with Et_2O (5 × 5 mL). The diethyl ether solution was washed with water (5 mL) to remove the remaining DMSO, and the organic phase was dried over $NaSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography with pentane : Et_2O mixtures of increasing polarity as eluants (first eluant: 90 : 10; for diketone isolation: 80 : 20). Compound **7**, a red solid with mp 93–95 °C was obtained in 12% overall yield from **11**. IR (CH_2Cl_2): 3050, 2986, 1683, 1485, 1266 cm^{-1}. ^{1}H NMR: δ 8.15 (dd, J = 7.8, 1.3 Hz, 1H, H–C8), 8.07 (B part of an AB system, J = 8.5 Hz, 1H, H–C1), 7.83 (A part of an AB system, J = 8.5 Hz, 1H, H–C2), 7.81 (dd, J = 7.8, 1.3 Hz, 1H, H–C6), 7.68–7.64 (m, 2H, H–C3′ and H–C4′), 7.63 (t, J = 7.8 Hz, 1H, H–C7), 7.34 (t, J = 8.9 Hz, H–C3″), 7.01 (t, J = 8.9 Hz, H–C4″), 6.97 (broad multiplet, 2H, hydrogen *meta* to F in phenyl ring), 6.72 (t, J = 8.0 Hz, 2H, hydrogens *ortho* to F in phenyl ring); ^{13}C NMR: δ 184.0, 142.3, 142.2, 139.2, 138.1, 137.8, 137.5, 135.7, 132.1, 130.8, 130.1, 130.0, 129.5, 129.4, 129.0, 128.8, 127.9, 127.3, 126.3, 122.7, 115.4; ^{19}F NMR: δ 117.0. $C_{24}H_{13}FO_2$ requires: C, 81.81; H, 3.72%; found: C, 81.59; H, 3.86%.

2D EXSY Experiments

For all the 2D EXSY experiments, the samples were dissolved in THF-d_8 and were degassed by several freeze–thaw cycles on a high vacuum line to remove dissolved oxygen. The spectra were recorded at ≤210 K temperature. Pure absorption 2D EXSY spectra were recorded employing the following parameters: spectral width 300 Hz; 256 time increments of 64 transients each; mixing times of 0.8 and 1 s for compounds, **1**–**3** and **4**–**7**, respectively; relaxation delays of 2.0 s (*ca*. 3 T_1 values of the relevant protons at the EXSY temperature).

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